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DEVELOPMENTS IN USSR WORK ON ADSORPTION

[Comment: Although a considerable amount of research dealing with physical adsorption is being conducted in the USSR, and new results in this field have been obtained (cf. the account of M. M. Dubinin's work below), increasing emphasis is being placed on the type of chemical adsorption which involves ion exchange and the use of ion-exchange agents (synthetic resins). There is a tendency to emphasize the specific, chemical aspects of adsorption processes on agents which hitherto have been regarded as purely physical and unspecific in their action (e.g., silica gel).

The reasons for the changed approach to the study of adsorption processes arise partly from the expansion of research and of practical work on industrial catalysts (i.e., agents on which highly specific processes of adsorption and desorption take place) and partly from current efforts to isolate on an industrial, semi-industrial, or analytical scale, substances which are present in very high dilutions. This applies to alkaloids, amino acids, antibiotics, and toxic agents present in the air. As far as toxic agents are concerned these can be analyzed after being concentrated by adsorption and must be adsorbed in any case to protect persons exposed to them. Research on adsorbents is very essential from the standpoint of work on gas masks leading to developments of the type [redacted]

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As far as work on atomic energy is concerned, the isolation and separation by adsorption of rare earth elements (with which thorium is frequently associated), transuranium elements, and radioactive isotopes is of importance. Some USSR work in this field is mentioned below. In addition to the old method of adsorptive coprecipitation, ion-exchange chromatographic separation of radioactive isotopes (A. K. Lavrukina), and of rare earths (D. I. Ryabchikov) is discussed by USSR investigators on the basis of work done in that country. In view of the fact that some rare earth elements are used as carriers in the isolation of radioactive isotopes by coprecipitation methods, USSR work on rare earth elements is also of significance from this standpoint.

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In the field of chromatography, the chromathermographic method described by Zhukhovitskiy et al., is of outstanding importance as an analytical procedure which appears to have nearly the same capabilities as mass spectrography (cf. R. H. Munch, "Vapor Phase Chromatography," Abstracts of Papers Presented at the 127th Meeting of the American Chemical Society, Cincinnati, 1955, p 8 B). Attempts to apply this method on an industrial scale as a means of separating and isolating substances present in a state of high dilution will bear watching. As indicated in an article by N. A. Izmaylov (see below), industrial installations for ion-exchange chromatographic separation and ion-exchange adsorption are definitely under consideration in the USSR and may already be in operation as far as the production of alkaloids is concerned. The designing of continuously working installations of this type and experimental work in that connection are significant, because ion-exchange resins can be used for the isolation and concentration of transuranium elements and radioactive isotopes.

Numbers in parentheses refer to appended sources.]

In reviewing the work done in 1954 by institutes of the Department of Chemical Sciences USSR, M. M. Dubinin, Academician-Secretary of the department, mentioned work on activated carbon adsorption and research on chromatography with the use of synthetic ion-exchange resins as chromatographic adsorbents. He also referred to the use of tracer atoms in work on adsorption phenomena. (See 00-W-31423.) Some of the work mentioned by Dubinin is discussed in greater detail below.

Activated Carbon

In an article dealing with the pore structure of activated carbons, M. M. Dubinin outlines research on this subject which has been conducted mainly by him and by his collaborators. The data obtained indicate that as far as the dimensions of the pores are concerned, activated carbons are neither monodisperse nor polydisperse systems, but exhibit a so-called polymodal distribution of pore sizes. This means that the curve of pore size distribution has a few relatively narrow and tall peaks. According to the data described, activated carbons in general have a tridisperse structure, i.e., their curves of pore size distribution exhibit three peaks which correspond to macropores, to pores of intermediate size, and to micropores. In view of the fact that in many types of carbon the volume of the intermediate pores is very small (less than 0.05 cubic centimeters per gram), these carbons constitute for all practical purposes bidisperse systems having only two varieties of pores, i.e., micropores and macropores. When such carbons are subjected to an activation which approaches the limiting degree, the micropores are enlarged to the size of intermediate pores. At the same time the macropores are also enlarged and a bidisperse carbon having only intermediate pores and macropores results. In a carbon of this type the specific surface of the adsorption film must for all practical purposes coincide with the specific surface corresponding to the pore contours.

According to Dubinin's treatment of the subject, carbons of the micropore type (first structural type) have a heightened adsorption potential, because the adsorption fields of the opposite walls of the micropores overlap. Such carbons have small micropores and their adsorption space is equal to the pore volume. Carbons of this type are best suited for the adsorption of gases and vapors.

In carbons of the second structural type, which have only large micropores or are practically devoid of micropores, the dimensions of the pores are not commensurate with the size of the molecules being adsorbed, as they are in carbons of the first structural type. Here the curvature of the surface exerts no influence on the adsorption, so that carbons of the second structural type

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do not differ in their properties with respect to adsorption from nonporous carbon adsorbents such as heat-treated carbon black. Carbons of the second structural type are best suited for decolorization, because the open pore structure of these carbons facilitates the entrance of large molecules and colloidal particles into the pores.

Carbons with a mixed pore structure intermediate between the first and second structural types are best suited for the recovery of products by adsorption because of the relatively easy desorption from these carbons.

Dubinin points out that the relationships and formulas pertaining to activated carbon which have been developed in his article also apply to other adsorbents such as silica gels, alumina gels, etc.(1)

Ion-Exchange Adsorbents

The subject of chromatography with the use of synthetic ion-exchange adsorbents is discussed in an article entitled "Cation-Exchange and Electron-Exchange Resins" by Ye. B. Trostyanskaya, I. P. Losev, and A. S. Tevlina. The use by Ye. N. Gapon, T. B. Gapon, and F. M. Shemyakin (Doklady Akademii Nauk SSSR, Vol 58, 1947, p 597) of a Permutit in the chromatographic separation of ions carried out for the first time is mentioned. According to the authors of the article, this Permutit was developed by the Institute of Applied Mineralogy. On the basis of articles that appeared in several collections of USSR published papers on chromatography which have been edited by Ye. B. Trostyanskaya and I. P. Losev, the authors describe the properties of synthetic cation-exchange resins of the carboxylic acid type, pointing out that these resins show a high selectivity of adsorption depending on the p_H and the valency of the ions being adsorbed. They also discuss phosphorylated cation-exchange resins and (on the basis of work by I. P. Losev and A. S. Tevlina) the properties of resins which in addition to adsorbing cations also reduce them. According to Losev and Tevlina, some reducing properties are possessed by phenol-formaldehyde resins, by all sorbents which have been modified by the introduction of acidic groups, and by all sulfonated polymers of styrene-containing substituents which form cross-links between the straight-chain polystyrene molecules. After describing the properties of resins which function both as cation-exchangers and reducing agents (i.e., electron exchangers), the authors discuss electron exchangers proper (i.e., resins which act as reducing agents but do not adsorb cations) on the basis of foreign publications.(2)

Chromatography

By applying a method of paper chromatography which uses small quantities of substance and is best suited for analytical determinations, V. L. Zolotavin of the Ural Polytechnic Institute imeni S. M. Kirov determined the order in which metal cations are adsorbed on aluminum hydroxide with which the paper had been impregnated. He also carried out separations, by this method, of several pairs of ions and of mixtures consisting of three ions.(3)

The chromathermographic method which has been developed by A. A. Zhukhovitskiy and members of his group involves passing of the mixture to be separated through a column of chromatographic adsorbent with simultaneous application of a temperature gradient. This method is used in prospecting for petroleum and natural gas. It also has general applicability for the concentration, determination, and isolation (potentially on an industrial scale) of substances which occur in a state of high dilution [redacted]

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Use of Chromatography and Other Adsorption Methods in the Isolation and Separation of Radioactive Isotopes

It is mentioned below that Izmaylov et al. refer to the separation of rare earth elements by means of ionic exchange resins. This subject is discussed in greater detail in a review article by D. I. Ryabchikov and Ye. A. Terent'yeva.(4) Elsewhere Ryabchikov in a communication from the Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy describes data demonstrating the applicability of the method of ion-exchange chromatography to the investigation of complex compounds (those of rhenium in this particular instance.(5)

A. K. Lavrukhina states that during 1953-54 research on elements occurring in ultrasmall quantities, i.e., radioactive isotopes, has been carried out at the Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, Academy of Sciences USSR, with the view of determining the behavior of these elements during precipitation, extraction, electrolysis, distillation, and ion-exchange chromatographic separation. She adds that data of this type are of importance for the isolation in a pure state (i.e., free of an admixture of carrier substances of radioactive elements obtained in nuclear reactions. The part of the investigation described in this instance deals with the precipitation together with hydroxides, sulfides, or some other compounds of the radioactive isotopes of Bi, I, Zr, Y, Ce, Fe, P, As, Co, Sb, Zn, and Nd, with particular attention to Bi^{210}. Ways of reducing the amount of the precipitated radioisotope by reprecipitation, increasing the acidity, or adding a complex-forming compound are also discussed.(6) The method of eliminating coprecipitation is illustrated in an article by N. A. Rudnev (also a contribution from the Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy) dealing with the prevention by means of basic dyestuffs of the coprecipitation of the radioactive thallium isotope Tl^{204} with arsenic trisulfide.(7)

Coprecipitation procedures are discussed by Lavrukhina on the basis of V. Khlopin's work. She says that it has been established at present that the following types of coprecipitation occur: isomorphic coprecipitation, coprecipitation by adsorption, formation of irregular mixed crystals, and internal adsorption in micro-fissures and microcapillaries. According to Lavrukhina, the adsorptive coprecipitation of radioisotopes with various precipitates is determined by the following factors:

1. The charge of the surface of the precipitate. Radioisotopes are effectively adsorbed by precipitates only when the charge of the surface of the precipitate is opposed to the charge of the ions of the radioisotope.

2. The solubility of the compounds being adsorbed. Results of experiments by Lavrukhina et al. on I^{131} and by A. Ratner on Pb^{212} show that as the solubility of the compound being adsorbed decreases, its adsorption by the precipitate increases. The solubility of the precipitate has no influence on the adsorption.

3. The surface of the precipitate. Precipitates consisting of small crystals are better adsorbents.

Khlopin's work on isomorphic precipitation is briefly reviewed by Lavrukhina.(6)

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Industrial Adsorption Processes and Chromatography

In an extensive article dealing with the application of adsorption processes in the isolation on an industrial scale of dissolved substances from solutions, N. A. Izmaylov, Yu. V. Shostensko, and S. Kh. Mushinskaya (Khar'kov) review this field mainly on the basis of their own work and of USSR publications on the subject (the bibliography, consisting of 71 titles, lists 9 foreign references and 62 USSR references). In the introduction to the article the authors give a brief survey of industrial processes of adsorption from solutions, pointing out that ion-exchange resins are being used for the separation of rare earth and transuranium elements and also for the isolation of copper, gold, and silver from dilute solutions of the salts of these metals. They also mention processes for the extraction of quinine, atropine, and scopolamine by means of cationites and procedures for the adsorption of salsoline, cytisine, and anabasine on bentonite.

The authors further point out that the technology of the adsorption of one substance from a solution is only a special case of the technology of chromatographic separation resulting in the isolation of several substances. They also state that N. A. Shilov, M. M. Dubinin, and their collaborators have developed a theory of the dynamic adsorption of gases, vapors, and their mixtures which forms the basis of the practical application of adsorption processes for capturing substances present in the form of vapors and gases in the air; that the basic postulates of this theory are applicable to adsorption from solutions as well; that further work on the dynamics of adsorption has been done by A. A. Zhukhovitskiy; that M. M. Dubinin et al. have recently achieved a considerable amount of success in work on the criteria of adsorbability of various substances on adsorbents of different structure; and that Ye. N. Gapon and B. N. Nikol'skiy have developed the theoretical fundamentals of the statics and dynamics of ionic chromatography.

After this introduction, the authors discuss in detail the advantages of adsorption from solutions as compared with extraction, the basic requirements which must be fulfilled by efficient technological adsorption processes, the adsorption on molecular adsorbents, the adsorption on ionic exchange agents, complete adsorption and desorption in stepwise processes and continuous processes, adsorption and desorption under dynamic conditions, and the regeneration of adsorbents. They point out that it is much easier to restore the activity of ionic exchange agents than that of molecular adsorbents and illustrate regeneration procedures with the example of adsorbents used in the production of alkaloids.

In conclusion the authors describe a technological scheme of a continuous counter-current adsorption-desorption procedure in which every adsorbent unit is replaced periodically by the following adsorbent unit in such a manner that the adsorbent moves in a closed cycle consisting of an adsorption stage, a desorption stage, and a regeneration stage. According to the authors, the process of dynamic adsorption which has been developed and described represents a continuously moving primary adsorption-column chromatogram in which the adsorption zone of one substance is continuously widened while the adsorption zones of all other substances are continuously displaced from the adsorbent as the current of the initial solution moves along. A characteristic trait of the procedure is that desorption is not carried out from a column consisting of a number of zones, but only from that part of the column in which the single substance that is being isolated is predominantly adsorbed. This form of chromatographic separation represents one of the possible solution of the problem

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in regard to the designing a continuously operating industrial chromatographic installation. The authors conclude this discussion by saying that the solution proposed by them in the terms outlined above can be extended to the case of the isolation of n substances. In that case the number of the required adsorption-desorption installations must be multiplied by n.(8)

Adsorption and Catalysis

The role of adsorption phenomena in heterogeneous catalysis is reviewed in the subdivision "Kinetics and Mechanism of Catalytic Reactions," a collection of papers dealing with problems to be discussed at the 1955 All-Union Conference on Chemical Kinetics and Reactivity. A paper by V. V. Voyevodskiy, F. F. Vol'kenshteyn, and N. N. Semenov discusses the adsorption of free atoms and radicals on the surface of catalysts and the adsorption of saturated molecules on catalyst surfaces with the formation of radicals. The crystalline catalyst is regarded as a gigantic radical which has free valencies on the surface. The authors point out that when the catalyst is treated as a radical, the difference between heterogeneous and homogeneous catalysis disappears.(9)

M. I. Temkin also emphasizes that the basic principle of catalytic activity is the same in homogeneous as in heterogeneous catalysis. He discusses the phenomena of heterogeneous catalysis from the standpoint of the interaction between activated atoms on the surface of the catalyst and treats the properties of gases adsorbed on metals in the light of results obtained in electrochemical investigations carried out by A. N. Frumkin and members of his group.(10)

In an article dealing with the activated state in catalysis, A. A. Balandin discusses activated adsorption from the standpoint of his multiplet theory.(11)

V. B. Aleskovskiy, in a paper dealing with the chemical structure of substances which act as adsorbents and are effective as heterogeneous catalysts, points out that catalysts remain unchanged during processes of catalysis and for that reason must be stable, i.e., high-molecular compounds. Conglomerates of small crystals would be too unstable to function effectively as catalysts notwithstanding their relatively large surface. Aleskovskiy postulates that adsorbents and catalysts consist of high-molecular, unsaturated, macroscopic radicals forming a skeleton and of a great number of functional groups covering this skeleton. These functional groups, although representing an insignificant fraction of the weight of the high-molecular substance, determine its behavior as a sorbent or catalyst, because they are attached at the active centers.

According to Aleskovskiy, the fact that silica gel powder acts as a radical can be demonstrated by heating potassium iodide or carbon tetrachloride with it. When this is done, liberation of iodine or chlorine, respectively, takes place at temperatures which are much lower than those necessary for the decomposition of the substances in question in the absence of silica gel powder.

On the basis of the experimental results obtained by him, Aleskovskiy concludes that catalysts must be pseudomorphous substances of the type of magnetic ferric oxide (gamma - Fe_2O_3), which is pseudomorphous with respect to magnetite (Fe_3O_4), having the same crystal structure as the latter. When in the course of catalytic oxidations (e.g., oxidation of hydrogen with oxygen) carried out in the presence of gamma-ferric oxide this oxide undergoes a reversible transformation into magnetite, it retains its original structure after reduction. This makes the gamma-ferric oxide an effective catalyst.

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By subjecting a ferric oxide catalyst to X-ray analysis during the process of flameless combustion of hydrogen with oxygen, Aleskovskiy found that oxide retains its crystal structure during the process of catalysis. When an excess of hydrogen is used, an admixture of Fe_3O_4 appears. Presence of an excess of oxygen results in a change in the structure of the catalyst: formation of a lattice of the corundum type takes place. When this happens, the catalyst loses its activity. However, the activity can be restored by treatment with hydrogen.

Extraction with acid sharply reduces the structural stability of the partly reduced oxide: it immediately assumes the corundum structure during flameless combustion of hydrogen and loses its activity. However, when potassium ions are introduced into the structure of the extracted catalyst, its structure and stability during the process of catalysis are noticeably strengthened.(12)

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